PB88-234034

Investigating the Fate of Dyes in the Environment

(U.S.) Environmental Research Lab., Athens, GA

Feb 88

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1. REPORT NO. EPA/600/M-88/013	2.	3. RE PB88-234034
4. TITLE AND SUBTITLE INVESTIGATING THE FATE OF DYES IN THE ENVIRONMENT (Trade Paper Version)		5. REPORT DATE February 1988 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) George L. Baughman* and Theresa A. Perenich**		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS *Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens GA 30613 **Department of Textiles, Merchandising, and Interiors, University of Georgia, Athens GA 30602		10. PROGRAM ELEMENT NO. ACULIA 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory - Athens, GA Office of Research and Develoment U.S. Environmental Protection Agency Athens, GA 30613		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

IN: American Dyestuff Reporter. 7(2):19-20,22,47-48, February 1988

16. ABSTRACT

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Reactions involving precipitation of Ca and Mg salts and ion exchange with sediments may be important for anionic and cationic dyes, respectively. The uncharged dyes are considered in regard to possible volatilization, sorption, and bioconcentration. Suitable kinetic and equilibrium constants are not currently available for quantitative prediction using mathematical models.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED 20. SECURITY CLASS *(This page)* UNCLASSIFIED	21. NO. OF PAGES 8 22. PRICE PC $9.95/MF $6.95

EPA Form 2220-1 (9-73)

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NATIONAL TECHNICAL
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SPRINGFIELD, VA 22161

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EPA/600/M-88/013

Investigating The Fate Of Dyes In The Environment

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Abstract

The rationale and approach that underlie use of mathematical models to forecast the environmental behavior of organic chemicals are examined. The general concepts are then used to show how knowledge of environmental and dye chemistry can be used to suggest pathways that are likely, or unlikely, to be determinants of dye fate in aquatic systems.

It is suggested that reactions involving precipitation of Ca and Mg salts and ion exchange with sediments may be important for anionic and cationic dyes, respectively. The uncharged dyes are considered in regard to possible volatilization, sorption, and bioconcentration.

It is noted that suitable kinetic and equilibrium constants are not currently available for quantitative prediction using mathematical models.

Introduction

Concerns about the impact of chemicals on the environment have been in the headlines the past 20 years and the situation has prompted the development of procedures for risk assessment. The implications of such procedures are important to manufacturers, users, and regulators of textile chemicals because of their bearing on the need, cost, and defensibility of environmental data. This is especially true of dyes, because of their wide geographic distribution and variable usage. This paper describes methods that are being used to investigate the fate of organic chemicals in the environment as part of the risk assessment process. Further, the benefits to be derived from a careful analysis of the fate of dyes and their behavior in the environment are examined. The focus of the paper has been to assemble information on environmental chemicals required in forecasting the environmental behavior of organic chemicals.

Risk Assessment: Procedures for assessing chemical risk to the environment are still not well defined and are currently the subject of intense research. Two main factors are involved in quantitative risk assessment: hazard and exposure. Hazard describes those indicators of potential biological effects, such as toxicity, carcinogenicity, etc., that have concentration and time dependencies, i.e., dose-response relationships. Exposure is the expected environmental concentration of a chemical over time and distance. Exposure assessment provides the impetus for developing data on the fate of chemicals. Data requirements depend on whether the risk being assessed is to humans, other specific biota such as fish, or the environment in general. Thus, knowledge of environmental transport and transformation (i.e., the fate of chemicals in the environment) is an essential component for casting biological test results in a realistic environmental scenario for the risk assessment process.

Hazard and exposure data provide information only about what is possible. The goal of risk or exposure assessment is to predict what is probable. When such assessments are properly conducted, they provide the best conclusions that can be attained given the available data. However, this neither implies that the assessments are always adequate nor that the conclusions will go unchallenged.

Assessment approaches

All environmental assessments, of either exposure or hazard, rely on both field and laboratory data, but various factors may dictate stronger reliance on one information source or the other. Hence, terminologies such as "field study" or "mathematical modeling" have evolved to indicate approaches that, respectively, are either more empirical or more conceptual. The major advantages and disadvantages of each approach will be discussed in regard to fate assessment (i.e., environmental exposure in natural waters).

When cost and time considerations permit, field studies present the approach of choice because they are often less controversial, can be tailored to a specific site, and can target the biota of most concern. Furthermore, field studies have high credibility with the public.

Besides being costly and time consuming, field studies may be affected by uncontrollable factors such as the amount of rainfall. Also, suitable methods of chemical or biological analysis may not be available for field studies, and interpretations can be complicated by the presence of other, possibly unknown, chemicals entering the study area. Another major limitation of field studies is that a defensible, explicit approach for extrapolating either data or conclusions to other chemicals or sites seldom exists.

An alternative to the highly empirical field study is the use of mathematical models and laboratory data. This approach is indicated when many different chemicals and different sites are to be considered, as often might be the case with dyes. Under such conditions, the only practical approach may be the use of mathematical models

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and laboratory data.

In this alternative approach, a water body is treated as a reactor with chemical input and output consisting of flow and chemical reactions. Thus, models such as EXAMS[1] account for loss of a chemical from the environment by chemical reactions such as hydrolysis, photolysis, microbial transformation, etc. Input data are values of the appropriate rate and equilibrium constants, as well as relevant properties of the environment such as pH, light intensity, etc.

The most widespread use of models is to provide a first approximation of environmental concentration as an evaluative tool. The result is not expected to predict precisely the conditions found in the real environment. Constants that are estimated from first principles, linear free energy relationships, etc., can be used. Equally important, environmental properties can be based on surveys of biota, historical records of meteorology and stream flow, or stochastic approaches. The characteristic of generality makes this approach useful and cost effective, when applicable.

An important argument advanced against use of models, as described, is lack of confidence in the approach on the part of persons unfamiliar with the details. Another objection has been related to the degree of accuracy required, because evaluative models are best in "forecasting" generalities. If predictions must be highly precise for a given compound in a specific environment, a large number of field measurements will be needed, especially in the environment of interest. Again we note that models and field measurements do not represent diametrically opposed approaches; they only reflect where the preponderance of effort will be required.

Environmental behavior of dyes

The processes most often included in models for predicting the behavior of organic chemicals in aquatic systems are shown in Table I, Bioconcentration is included in the table because of its importance, but it is seldom a significant factor in reducing the dissolved concentration. Additional processes that may be important for dyes include ionization, abiotic oxidation, abiotic and microbial reduction, precipitation, and ligand exchange.

An important characteristic of all dyes is their ionic state; for all practical purposes ionic compounds are nonvolatile. Therefore, volatilization will not be important for the acid, direct, basic, and metal complex dyes or for most fluorescent brightening agents. In principle, the solvent, disperse, vat, and sulfur dyes have the potential to be volatile. Vapor pressure data are not available for most dyes, but the sulfur dyes, vat dyes, and neutral fluorescent brightening agents are large, complex molecules that can be expected to have vapor pressures lower than the disperse dyes.

Data in the literature demonstrate that the vapor pressures of the older disperse dyes are quite low. The newer, "high energy" dyes are likely to be less volatile, although this conclusion is based on chemical structure rather than actual vapor pressure data. Taken alone, vapor pressure does not establish that volatilization is an insignificant pathway for dye loss from water, but simple comparison is likely to be qualitatively correct. Table II presents vapor pressures for several dyes; the same applies for some chemicals that have been studied in the environment.

Table I: Processes most often included in models for predicting behavior of organic chemicals in aquatic systems.

Process	Usual Treatment
Volatilization	kinetic
Sediment sorption	equilibrium
Photolysis	kinetic
Hydrolysis	kinetic
Biolysis (bacterial transformation)	kinetic
Bioconcentration	equilibrium

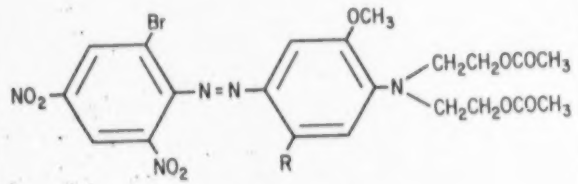
Table II: Vapor pressures (m.m.Hg) of some dyes and other chemicals at 25°C.

Compound	Vapor pressure	Reference
1-(2-hydroxyethylamino) anthracene 9,10 dione	1.2×10^{-11}	2
4(N,N dimethylamino) azobenzene (Solvent Yellow 2) CI 11020	3.6×10^{-9}	3
4-nitro-4'-aminoazabenzene (Disperse Orange 3) CI 11005	1.9×10^{-11}	3
4(N,N dimethylamino) 5 methyl 4'nitroazabenzene	1.0×10^{-9}	3
1-methylamino-anthracene 9,10-dione (Disperse Red 9) CI 60505	1.2×10^{-8}	4
4(N-2-hydroxyethyl-N-ethylamino) 4'nitroazobenzene (Disperse Red 1) CI 11110	2.3×10^{-13}	4
1,4,5,8 tetraaminoanthracene 9,10- dione (Disperse Blue 1) CI 64500	1.8×10^{-8}	5
1,4 dihydroxyanthracene 9,10-dione	1.1×10^{-9}	5
Indigo (Vat Blue 1) CI 73000	8.3×10^{-13}	6
Mikethren Blue RSN (Vat Blue 4)	1.9×10^{-18}	6
DDT	1×10^{-7}	7
Dieldrin	1×10^{-7}	7
Di(2-ethylhexyl)phthalate	2.4×10^{-7}	8

A final reason why volatilization is unlikely to be important for the uncharged dyes is that the escaping tendency or fugacity that drive volatilization is also the driving force for both sorption and bioconcentration. Because the aquatic system contains so much sorbent in the form of sediment and biomass, the rate of volatilization will be reduced in proportion to the extent that these pathways reduce the dissolved concentration. Use of fugacity to describe sorption equilibria and volatilization kinetics has been extensively studied by Mackay.[7,8]

Interestingly, among the few environmental studies of dyes are two that show the occurrence of these pathways. The first, a study by Jensen et al., demonstrates bioconcentration of a fluorescent

Figure 1—Dye with multiple functional groups.



brightener, and the second, by Tincher[11], reports much higher concentrations of acid and disperse dyes in sediment than in surrounding water.

Sorption of dyes should reasonably be expected to be important in the environment because dyeing itself is a sorptive process. Based on the properties of sediments, cation exchange is anticipated to be extensive and rapid for the basic dyes. A similar situation should exist for acid and direct dye anions, but the equilibrium constants would probably be much smaller. Surprisingly, sediment has not been studied more in the environment or even in the laboratory. It is all the more surprising when one recognizes that equations developed to describe the behavior of chemicals in the environment are the same as those used to describe fiber sorption.

With the exception of Tincher's work[11], and several studies of anionic fluorescent brighteners (FWAs), there is little literature on the environmental behavior of dyes. As described, this is probably because environmental work depends heavily on gas chromatography/mass spectroscopy, and this technique is not suitable for most dyes due to their lack of volatility. Unfortunately, no other suitable analytical methods are available for dyes in general and the ionic dyes in particular. Unless it is necessary to identify dyes, liquid chromatography will increasingly be a tool of choice, as demonstrated by Tincher's work.[11]

Hydrolytic reactions, whether chemically or microbially mediated, will probably not be very important, i.e., not fast. This conclusion is based on the fact that if the dye is not broken down during the rigors of biological waste treatment, it is unlikely to biograde rapidly in the less severe conditions of the environment. Also, most dyes have few readily hydrolyzable functional groups in positions such that the central resonance structure of the molecule would be disrupted by their removal. For example, hydrolysis of one or more acetyl groups, as shown in Figure 1, may not change a measured biological endpoint such as toxicity. It would probably have a large effect on biological availability and fate, however.

Photochemical transformation is another pathway that might be anticipated to be important for dyes because these compounds are excellent absorbers of solar energy. Yet, any study of this pathway under environmental conditions has also received little attention. Because dyes have been designed for light fastness, it is interesting that Haag and Mill[12] suggest that direct photolysis will be much slower than indirect photolysis in natural waters where reactive species can form from other components, such as humic materials.

It has also been found that certain compounds, among them dyes, are activated by light with a resulting significant increase in toxicity. This phenomenon was of sufficient interest to be the subject of a recent symposium on its possible pesticidal applications (Agrochemical Division, 192nd American Chemical Society meeting, Anaheim, Ca., Sept. 7-12, 1986).

Table III: Effect of Salt Formation on Solubility

Compound	Solubility(gm/l)	T(C)	Ref.
1,5 anthraquinone disulfonic acid.4H2O	660	18	15
Mg 1,5 anthraquinone disulfonate.8H2O	20.4	18	16
Ca 1,5 anthraquinone disulfonate.3H2O	9.1	18	16
1,8 anthraquinone disulfonic acid .5H2O	660	18	15
Mg 1,8 anthraquinone disulfonate .6H2O	10	18	15
Ca 1,8 anthraquinone disulfonate .51/2H2O	0.7	18	16
2-Naphthalene sulfonate	679	30	15
Mg 2-Naphthalene sulfonate	69.8	17	16
Ca 2-Naphthalene sulfonate	19.8	16.5	16

It has been known for some time that fluorescent brightening agents of the stilbene type undergo *cis-trans* isomerization in light,[13] a process that has been suggested as a loss mechanism in a Japanese river.[14] The only known environmental significance of this reaction is its implications for chemical analysis.

Reaction of organic ions is another pathway that has received little attention from environmental researchers. Although the scientific basis exists in many cases, most models do not contain algorithms suitable for assessment. Also, few of the equilibrium constants have been published although some of these reactions are the source of well known problems for the dyer (e.g., reaction of ionic dyes with detergents, metals, or other dyes of opposite charge).

It is almost certain that some of these reactions will be operative in aquatic systems. One would expect anionic dyes to react with Ca, Mg, etc. to form highly insoluble salts (i.e. pigments) and thereby reduce the concentration available for other reactions or biological effects. Table III shows the effect of salt formation on solubility of a few simple compounds. A similar result can be anticipated for basic dyes due to their interaction with humic materials and hydrous oxides. The importance of equilibrium constants for calculating the actual dissolved dye concentration, hence the effect of dyes on the aquatic system, should be obvious. Except for some work on reaction of cationic and ionic detergents, there are no published data on either the kinetics or the equilibria of these reactions.

Ion-pair formations is a related process that has implications for large organic ions but which, again, has been neglected in the environmental context although

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its analytical applications are well known. Such reactions would be expected to influence any partitioning phenomenon like bioconcentration or hydrophobic sorption—cf. pentachlorophenol.[17] Dye molecules are excellent subjects for such studies.

A final category that should be considered is redox reactions. Microbial reduction was used in early vat dyeing before replacement by chemical reactants. Also, many of the dyes are well known to be reversibly oxidized, sometimes by air. Based on dye chemistry alone, it seems likely that this process will be important to the fate of certain dyes if they are present in aquatic systems.

Reduction in the environment is expected to occur under anaerobic conditions most likely to be found in bottom sediments. The difficulties of working with anaerobic systems, however, has strongly affected our knowledge of both the microbiology and chemistry of environmental reduction reactions.

Only recently have reactions in anaerobic sediments begun to receive attention, and there are now some reports of abiotic reduction of nitro and azo groups.[18-20] There are also reports of microbial transformation of azo dyes but most studies were conducted under pure culture or waste treatment conditions. Indeed, some of the environmental questions about dyes stem from the concern that azo dyes may be reduced to the starting materials (e.g. benzidine). Whether the formation of a small amount of hazardous compound is more desirable than the destruction of a large portion of the dye is a question that can only be objectively assessed when kinetic, equilibrium and biological are available.

Conclusions

There is sufficient knowledge of dye chemistry to permit defensible identification of many of the reactions that are likely to determine dye fate in natural waters. Unfortunately, few data on the chemistry or microbiology of dyes are published for conditions outside the dye bath. This is especially true of data on rate and equilibrium constants of the type needed to forecast environmental concentration and biological impacts.

It is unrealistic to think that such data for most dyes can, or, in many cases, ever will be generated, especially in the environment. Thus, the most reasonable approach is to compile data on compounds that possess selected chemical properties which can then be used to predict the properties and environmental behavior of many others. □ □ □

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